

18 OCT 2003

1,0/530092

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
18 March 2004 (18.03.2004)

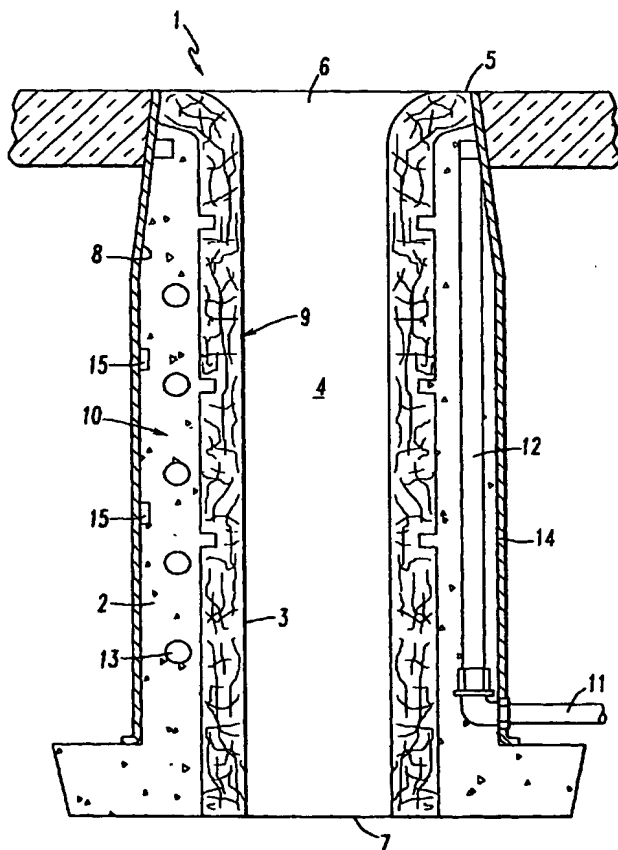
PCT

(10) International Publication Number
WO 2004/022267 A1

- (51) International Patent Classification⁷: **B22D 41/54**, 41/58
- (21) International Application Number: PCT/US2003/027209
- (22) International Filing Date: 2 September 2003 (02.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/407,815 3 September 2002 (03.09.2002) US
- (71) Applicant (for all designated States except US): **VESUVIUS CRUCIBLE COMPANY** [US/US]; 103 Foulk Road, Wilmington, DE 19803 (US).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): **RICHAUD, Johan** [FR/CA]; 6 Waterwheel Crescent, Dundas, Ontario L9H 7B6 (CA).
- (74) Agent: **SATINA, Donald, M.**; Jamison, Seltzer, Harper & Williams, 2625 Wilmington Road, New Castle, PA 16105 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: GAS PURGED NOZZLE



(57) Abstract: A nozzle (1) is described for delivering a flow of liquid metal from a metallurgical vessel. In combination with inert gas, the nozzle can shield the flow of liquid metal from oxygen and, additionally, can be used to purge liquid metal residing in the metallurgical vessel. The nozzle includes a substantially gas-impermeable liner (9) surrounded by a permeable composition (10). The gas-impermeable liner may comprise a resin-bonded material, and the permeable liner is preferably a carbon-bonded or castable refractory. A metal housing (14) may surround the nozzle.

WO 2004/022267 A1



European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations* AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO

patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

- *of inventorship (Rule 4.17(iv)) for US only*

Published:

- *with international search report*
- *with amended claims and statement*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

FIELD OF THE INVENTION

This invention relates to a refractory nozzle for use in the casting of molten steel, and particularly to a nozzle that uses inert gas for reducing unwanted
5 accumulation of alumina deposits at the steel/nozzle interface.

BACKGROUND OF THE INVENTION

Refractory articles for controlling a flow of molten metal, such as steel, are known in the prior art. Such articles include nozzles, slide gate plates, stopper rods and shrouds, and are often used in combination to modulate a flow of liquid steel
10 during the casting of molten metal. In the 1970's, the manufacture of aluminum-killed steels became one of the most common products of the steel making industry due to their desirable metallurgical properties. Unfortunately, alumina and other refractory compounds deposit and accumulate at the interface of the article and the molten steel. Interfaces include, for example, the bore and top surface of the nozzle.
15 Such deposits can ultimately cause the complete blockage of the nozzle or prevent shut-off of flow of the molten steel.

Inert gas has been used to reduce unwanted deposits on refractory surfaces. Nozzle assemblies frequently include porous, gas-conducting refractory elements. Gas delivery systems, such as channels, grooves or devices, within or outside the
20 nozzle can direct inert gas to the porous elements. Examples of such nozzles are U.S. Pat. Nos. 4,360,190; 5,100,035, 5,137,189, and 5,723,055. In operation, a pressurized inert gas, such as argon, travels through the gas delivery system and percolates through the porous refractory elements. The porous elements may define at least a portion of the bore surface or may be proximate to the bore surface so that inert gas

may escape into the bore. Additionally, the porous element may be near or at the top surface of the nozzle. The resulting flow of small argon bubbles through the sides of the bore or top surface of the nozzle can reduce the deposition of unwanted alumina in these areas.

5 Research has shown that oxygen reacts with constituents in the nozzle and the molten steel to produce alumina deposits. By injecting an overpressure of inert gas, the prior art decreased the partial pressure of oxygen available to cause clogging. In other words, the prior art injected inert gas into the nozzle and subsequently into the stream of molten steel causing a reduction in oxygen concentration and corresponding
10 reduction in unwanted deposits. This solution is not entirely satisfactory because oxygen is still present to the molten steel because of, for example, leaks in the inert gas system, contamination of the inert gas, and preexisting oxygen in the system. Clogging can still occur.

 A need exists for a refractory article that shields the molten steel from oxygen.
15 Prior art articles still permit the diffusion of oxygen through the article and into the molten steel. Metal cans have not proven completely acceptable because oxygen can still penetrate along the interface between the article and the can. Furthermore, "canning" significantly adds to the expense of the product. Ideally, a nozzle would scavenge or scrub oxygen from the inert gas while imposing an impermeable barrier
20 around the molten metal.

SUMMARY OF THE INVENTION

The present invention describes a refractory article for use in the casting of molten steel that reduces the accumulation of inclusions, particularly alumina, on surfaces exposed to a stream of molten steel. Surfaces may include the bore or top

surface of a nozzle.

In a broad aspect, the article includes a liner comprising a substantially gas-impermeable refractory composition and a gas-permeable refractory composition surrounding the liner. The impermeable composition inhibits oxygen diffusion to the molten metal. The permeable composition is adapted to permit diffusion of inert gas, thereby shielding the impermeable composition and the molten metal from oxygen.

The impermeable composition is preferably a resin-bonded composition comprising a refractory aggregate, binder and oxygen getter. The latter includes compounds that scrub oxygen from the gas entering the molten metal, and includes reactive metals.

The gas-permeable composition may comprise carbon-bonded, oxide-bonded, resin-bonded, or castable refractories. Importantly, the permeable composition permits the diffusion of inert gas so that inert gas substantially shields the impermeable composition and the molten metal from oxygen ingress. Conveniently, the porosity of the permeable composition can control the diffusion of inert gas. Alternatively or in conjunction with porosity, a gas delivery system, such as channels, grooves or devices, may facilitate the delivery and diffusion of inert gas through the permeable material.

The method of the present invention includes lining a bore of a refractory article with a substantially gas impermeable composition, surrounding at least a portion of the impermeable composition with a gas-permeable composition, and flooding the permeable composition with inert gas.

In one embodiment, an overpressure of inert gas shields the molten metal from oxygen. In an alternative embodiment, the inert gas purges molten metal within a

metallurgical vessel.

BREIF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a cross-section of a refractory nozzle of the present invention.

Figure 2 shows an alternative embodiment that permits purging of molten

5 metal in a metallurgical vessel.

DETAILED DESCRIPTION OF THE INVENTION

The present invention concerns refractory articles used to control the flow of molten metal, specifically steel. The present invention may include any refractory article for conducting a flow of molten metal, including nozzles, shrouds and slide
10 gate plates. For convenience, nozzle shall mean any refractory article used to conduct a flow of molten metal.

Figure 1 shows one embodiment of the present invention. The article 1 comprises a nozzle body 2 having an inner surface 3 defining a bore 4, a top surface 5 surrounding an inlet 6 of the bore 4, an outlet 7 fluidly connected to the inlet 6, and an
15 outer surface 8. The bore 4 is adapted to transfer the steel from the inlet 6 to the outlet 7. The inner surface 3 includes a liner 9 comprising a substantially gas-impermeable composition. The liner 9 defines at least a portion, and preferably all, of the bore 4. An outer portion 10 of the nozzle 2 surrounds the liner 9 and comprises a gas-permeable composition. The nozzle 2 is adapted to receive a flow of inert gas.
20 During casting, a conduit 11 may deliver the gas to the nozzle 2 and, in combination with various channels, grooves or devices 12 within or surrounding the nozzle 2, the gas permeates the outer portion 10 effectively shielding the molten metal in the bore 4 from the atmosphere.

The gas-impermeable composition must be substantially impermeable to

gases. One skilled in the art is aware of several methods to produce an impermeable material using a variety of chemical and mechanical means. For examples, fluxes, glazes, particle size distribution, bonding system, composition of the refractory, and processing conditions can individually and in combination affect permeability.

- 5 Fluxes lower the glass temperature and facilitate vitrification. Glazes produce an impervious coating on the surface of the refractory. Particle size distribution in a refractory aggregate can substantially affect porosity, and ultimately permeability, in a finished product. Processing conditions, such as firing temperature and pressing, have profound effects on permeability. Chemical compositions of the refractory and
- 10 bonding system also substantially affect permeability.

The gas-impermeable composition may be formed from any type of material, including resin-bonded, carbon-bonded, oxide-bonded, and castable refractories.

- Carbon-bonded refractories include mixtures of refractory aggregate, graphite and a binder that have been fired under reducing conditions. Firing means heating the
- 15 composition at a temperature capable of forming metal carbides, particularly aluminum carbide. Such temperatures are typically above 800°C, but may be higher depending on the firing time. Oxide-bonded compositions are sintered at elevated temperatures, often substantially higher than temperatures needed for carbon-bonding. Resin-bonded refractories are cured at temperatures below about 800°C, and
- 20 frequently below about 500°C. Unlike the previous materials, castable refractories do not typically need pressing and can be molded at near ambient temperature and pressure. A castable material includes any of the refractory cement-like products commonly used in the industry.

In a preferred embodiment, the impermeable composition comprises a resin-

bonded material. Such materials require no special processing or chemicals, and are familiar to manufactures of refractories for the steel industry. Advantageously, resin-bonded compositions are cured at low temperatures, can comprise clog-resistant materials, and may contain oxygen getters that would not survive high temperature firing needed for carbon-bonded or oxide bonded materials.

Suitable resin-bonded compositions include at least one refractory aggregate, a curable resin binder and a reactive metal. Refractory aggregate includes any refractory material suitable for steel casting, including but not limited to alumina, magnesia, calcia, zirconia, silica, compounds and mixtures thereof. Preferably, compounds that can produce volatile oxides at elevated temperatures, such as silica and magnesia, should be avoided because volatile oxides are a means of oxygen transport to the molten metal, and oxygen ingress has been correlated with alumina deposition.

The curable resin binder should be present in an amount to achieve adequate green strength after pressing and curing. Curing commonly occurs at below around 300 °C. The composition may be heat treated at a temperature preferably below about 800°C and most preferably below about 500°C. The amount of binder will vary depending on, for example, the type of binder used and the desired green strength. A sufficient amount of binder will typically be from 1-10 wt.%. Typically, the binder is organic and usually the binder is a carbon resin, such as, a carbonaceous binder derived from pitch or resin. The binder may include other types of organic binders, such as, phenolic compounds, starch, or ligno-sulfinate.

The gas-impermeable composition may also comprise oxygen getter. An oxygen getter reacts with oxygen that diffuses into or forms within the gas-

impermeable composition, thereby making the oxygen unavailable to the molten steel.

Common oxygen getters include, for example, boron compounds, carbides, nitrides, and reactive metal powders such as aluminum, magnesium, silicon and mixtures and alloys thereof. Advantageously, boron compounds reduce porosity and permeability,

5 thereby creating a physical barrier to oxygen diffusion. The needed quantity of oxygen getter depends on the particular use to which the refractory article will be placed. A minimum of 0.25 wt.% is believed necessary to show demonstrable improvement in oxidation-resistance. Alternatively, more than 15 wt.% is costly, typically unnecessary, and may even be hazardous such as when using reactive metal
10 powders. Additionally, oxygen getters may decrease thermal shock-resistance of the fired shape and reduce erosion-resistance to steel.

A preferred oxygen getter comprise reactive metals, including aluminum, magnesium, silicon, titanium, and mixtures and alloys thereof. Conveniently, reactive metals are added as powders, flakes and the like. The reactive metal should be

15 present in sufficient quantity so that, during casting of molten steel, the reactive metal scavenges any oxygen that may diffuse into or emanate from the refractory article.

Various factors affect the amount of reactive metal that will be sufficient to scavenge oxygen. For example, the inclusion of oxygen-releasing compounds, such as silica, require higher levels of reactive metal in order to scavenge the released oxygen.

20 Limitations on the amount of reactive metal include cost and hazardousness.

Reactive metals are generally more expensive than refractory aggregates and, especially as powders, reactive metals can be explosive during processing. A typical amount of reactive metal is from 0.5-10 wt.%.

The impermeable composition may include a resin-bonded composition

comprising 50-90 wt.% refractory aggregate, 1-10 wt.% binder, and 0.5-15 wt.% reactive metal. More preferably, the resin-bonded composition comprises 65-80 wt.% fused alumina, 2-30 wt.% calcined alumina, 1-10 wt.% binder, 0.5-10 wt.% aluminum metal, up to 15 wt.% zirconia, and less than 3 wt.% silica.

5 The gas-permeable refractory composition may comprise any suitable refractory composition, including carbon-bonded, oxide-bonded, resin-bonded, or castable refractories, but preferably comprises carbon-bonded refractories or castable materials. Suitable carbon-bonded refractories are well known by one skilled in the art, and typically are thermal shock resistant. Castable materials are commonly dry
10 powders that are mixed with water to form a slurry. Advantageously, the slurry can be molded around the impermeable composition without pressure or temperature extremes.

 The permeable composition should surround at least a portion of the impermeable composition, and preferably it surrounds the entire impermeable
15 composition. Desirable, but not necessary, features of the permeable composition include easy grindability and low thermal conductivity compared to the impermeable composition. Grindability permits easier machining of a refractory article to its finished dimension. Low conductivity insulates the molten steel and reduces the likelihood of steel freezing in the nozzle.

20 The permeable composition permits the diffusion of inert gas so that inert gas substantially shields the impermeable composition and the molten metal from oxygen ingress. Conveniently, the porosity of the permeable composition can control the diffusion of inert gas. As explained above, one skilled in the art is aware of numerous techniques to increase porosity. Fugitive additives, such as waxes and volatile

compounds, may also be used to increase porosity. Alternatively or in conjunction with porosity, a gas delivery system, such as channels, grooves or devices, may facilitate the delivery and diffusion of inert gas through the permeable material.

Porosity of the refractory largely controls permeability. Total porosity of the gas-permeable composition should be at least about 15%. Alternatively, the gas-permeable composition should have a porosity at least about 5% greater than the gas-impermeable composition. The difference in porosities is sufficient to channel gas through the permeable composition and away from the impermeable composition.

Contiguous, open-cell pores are particularly effective at increasing permeability. Gases can readily travel from pore to pore without impediment. Large pore size also facilitates gas transport. In contrast, small pore size requires greater pressure to infuse the permeable composition with gas. Large pores, of course, can decrease the strength of the material. Preferably, the average pore size of the gas-permeable refractory is at least about one micron and less than five millimeters.

Gas delivery systems can increase gas transport. Such systems comprise channels, grooves or devices within or on a surface of the refractory article. Figure 1 shows a device 12 within the article. The device can be perforated to permit uniform distribution of gas along its length. Channels 13 on the interior of the nozzle 2 perform a similar function. Channels are frequently produced by burning out wax or other low melting point material that had been pressed or cast into the refractory article.

A metal can 14 may be used with the refractory article, especially when the article is a collector nozzle of a ladle or tundish. A metal can 14 often improves physical integrity and creates a mechanical barrier to oxygen diffusion. An added

benefit is the ability to create a gas channel from a groove 15 on the outer surface 8 of the nozzle 2 and the metal can 14. Such grooves are often easier to manufacture than gas channels within the refractory article.

Figure 2 shows an alternative embodiment of the present invention. A

5 subentry nozzle 2 extends from an interior volume 21 of a tundish 20 to a mold 22. The nozzle 2 comprises an impermeable liner 9 surrounded by a permeable composition 10. The nozzle 2 includes a top surface 5 surrounding the inlet 6. Unlike Figure 1, the permeable composition 10 extends to the top surface 5. Forcing inert gas through the permeable composition 10 at a pressure higher than the
10 ferrostatic head can force the gas to exit the top surface 5, thereby purging the molten metal within the tundish 20. Obviously, purging can also be accomplished with a well nozzle of appropriate construction.

The impermeable and permeable compositions should form a single refractory article. The compositions may be co-pressed; one composition may be formed
15 around or within the other composition; or pieces comprising first and second compositions may be joined together, such as by mortaring. Co-pressing is useful when the first and second compositions are particulates, and is particularly useful when the compositions require similar processing, such as, curing cycles, for example, when both compositions are resin-bonded compositions.

20 Pressing includes isostatic and standard, uniaxial pressing. Co-pressing is also possible when one composition is pressed with a preform piece of the other composition. For example, a material may be pressed and fired to form a permeable, carbon-bonded preform. A second material, which will form the impermeable composition, can then be pressed and cured with the permeable preform to form the

refractory article.

Alternatively, an impermeable composition may be pressed and a permeable material may be molded in or cast around the second material. In one such embodiment, a slide gate plate may have a liner comprising the impermeable material and a porous castable material may comprise the remainder of the plate. Another method of combining first and second compositions includes joining a first piece comprising an impermeable composition to a second piece comprising a permeable composition. Typically, a refractory mortar is used to join the two pieces.

The method of the present invention includes lining a bore of a refractory article with a substantially gas impermeable composition, surrounding at least a portion of the impermeable composition with a gas-permeable composition, and flooding the permeable composition with inert gas.

In one embodiment, as shown in Figure 1, an overpressure of inert gas shields the molten metal from oxygen. In an alternative embodiment, as shown in Figure 2, the inert gas shields molten metal within the bore from oxygen and purges molten metal within a metallurgical vessel.

Obviously, numerous modifications and variations of the present invention are possible. It is, therefore, to be understood that within the scope of the following claims, the invention may be practiced otherwise than as specifically described. While this invention has been described with respect to certain preferred embodiments, different variations, modifications, and additions to the invention will become evident to persons of ordinary skill in the art. All such modifications, variations, and additions are intended to be encompassed within the scope of this patent, which is limited only by the claims appended hereto.

What is claimed:

1. A refractory nozzle for use in the casting of molten metal having an inlet, an outlet fluidly connected to the inlet, an outer surface, an inner surface defining a bore between the inlet and the outlet, and a top surface surrounding the inlet, the nozzle adapted to receive a flow of inert gas and characterized by:
 - a) a substantially gas-impervious refractory composition lining at least a portion of the inner surface; and
 - b) a gas-permeable refractory composition surrounding at least a portion of the gas-impervious composition, the permeable composition having a porosity sufficient to permit diffusion of inert gas.
2. The refractory nozzle of claim 1, further characterized by the gas-permeable composition having a porosity of at least 15%.
3. The refractory nozzle of any one of the preceding claims, further characterized by the permeable composition including an open-cell pore structure and an average pore size of at least one micron.
4. The refractory nozzle of any one of the preceding claims, further characterized by the permeable refractory composition selected from the group consisting of carbon-bonded refractories, oxide-bonded refractories, resin-bonded refractories, castable refractories and mixtures thereof.
5. The refractory nozzle of any one of the preceding claims, further characterized by the gas-impervious refractory composition selected from the group consisting of carbon-bonded refractories, oxide-bonded refractories, resin-bonded refractories, castable refractories and mixtures thereof.
6. The refractory nozzle of any one of the preceding claims, further characterized

by the gas-impervious composition including oxygen getters.

7. The refractory nozzle any one of the preceding claims, further characterized by the gas-impervious composition comprising a resin-bonded refractory comprising 50-90 wt.% refractory aggregate, 1-10 wt.% binder, and 0.5-15 wt.% reactive metal.

8. The refractory article of claim 7, further characterized by the refractory aggregate comprising at least one refractory material selected from the group consisting of alumina, zirconia, calcia, magnesia, silica, and mixtures and compounds thereof.

9. The refractory nozzle of any one of claims 7 and 8, characterized by the reactive metal comprising at least one metal selected from the group consisting of aluminum, magnesium, silicon, titanium, and mixtures and alloys thereof.

10. The refractory article of any one of the preceding claims, characterized by the gas-impervious refractory composition made from a mixture comprising 65-80 wt.% fused alumina, 2-30 wt.% calcined alumina, 1-10 wt.% binder, 0.5-10 wt.% aluminum metal, up to 15 wt.% zirconia, and less than 3 wt.% silica.

11. The refractory nozzle of any one of the previous claims, further characterized by the nozzle including an inert gas delivery system.

12. The refractory nozzle of claim 11, characterized by the gas delivery system being selected from the group consisting of channels, grooves and devices.

12. The refractory nozzle of any one of the preceding claims, further characterized by a metal housing at least partially encasing the outer surface of the nozzle.

13. The refractory nozzle of any one of the preceding claims, further characterized by the permeable composition extending to the top surface, whereby inert gas

can purge the molten metal when pressure of the inert gas exceeds ferrostatic head in the molten metal.

AMENDED CLAIMS

**[Received by the International Bureau on 03 February 2004 (03.02.04):
original claims 1 – 13 replaced by amended claims 1 - 14
(2 pages)]**

+ Statement

WHAT IS CLAIMED IS:

1. A refractory nozzle for use in the casting of molten metal having an inlet, an outlet fluidly connected to the inlet, an outer surface, an inner surface defining a bore between the inlet and the outlet, and a top surface surrounding the inlet, the nozzle adapted to receive a flow of inert gas and characterized by:
 - a) a gas-impervious refractory composition lining substantially the entire inner surface; and
 - b) a gas-permeable refractory composition surrounding at least a portion of the gas-impervious composition, the permeable composition having a porosity sufficient to permit diffusion of inert gas.
2. The refractory nozzle of claim 1, further characterized by the gas-permeable composition having a porosity of at least 15%.
3. The refractory nozzle of any one of the preceding claims, further characterized by the permeable composition including an open-cell pore structure and an average pore size of at least one micron.
4. The refractory nozzle of any one of the preceding claims, further characterized by the permeable refractory composition selected from the group consisting of carbon-bonded refractories, oxide-bonded refractories, resin-bonded refractories, castable refractories and mixtures thereof.
5. The refractory nozzle of any one of the preceding claims, further characterized by the gas-impervious refractory composition selected from the group consisting of carbon-bonded refractories, oxide-bonded refractories, resin-bonded refractories, castable refractories and mixtures thereof.
6. The refractory nozzle of any one of the preceding claims, further characterized by the gas-impervious composition including oxygen getters.

7. The refractory nozzle any one of the preceding claims, further characterized by the gas-impervious composition comprising a resin-bonded refractory comprising 50-90 wt.% refractory aggregate, 1-10 wt.% binder, and 0.5-15 wt.% reactive metal.
8. The refractory article of claim 7, further characterized by the refractory aggregate comprising at least one refractory material selected from the group consisting of alumina, zirconia, calcia, magnesia, silica, and mixtures and compounds thereof.
9. The refractory nozzle of any one of claims 7 and 8, characterized by the reactive metal comprising at least one metal selected from the group consisting of aluminum, magnesium, silicon, titanium, and mixtures and alloys thereof.
10. The refractory article of any one of the preceding claims, characterized by the gas-impervious refractory composition made from a mixture comprising 65-80 wt.% fused alumina, 2-30 wt.% calcined alumina, 1-10 wt.% binder, 0.5-10 wt.% aluminum metal, up to 15 wt.% zirconia, and less than 3 wt.% silica.
11. The refractory nozzle of any one of the previous claims, further characterized by the nozzle including an inert gas delivery system.
12. The refractory nozzle of claim 11, characterized by the gas delivery system being selected from the group consisting of channels, grooves and devices.
13. The refractory nozzle of any one of the preceding claims, further characterized by a metal housing at least partially encasing the outer surface of the nozzle.
14. The refractory nozzle of any one of the preceding claims, further characterized by the permeable composition extending to the top surface, whereby inert gas can purge the molten metal when pressure of the inert gas exceeds ferrostatic head in the molten metal.

STATEMENT

Applicant has amended the claims to correct typographical errors and to clarify the distinction between the present invention and the prior art.

As amended, the nozzle comprises a gas permeable composition surrounding at least a portion of a gas-impervious composition, which makes up an inner surface of the nozzle. In contrast, the cited prior art teaches an impermeable liner over only a fraction of the inner surface.

The nozzle of the present invention comprises a gas-impervious composition that defines a bore through which the molten metal may flow. This configuration simultaneously shrouds the nozzle with inert gas and shields the molten metal from gas of any type. Prior art does not teach or suggest this feature of the invention.


Prior art directs gas into the molten metal at defined locations along the nozzle. For example, US 5723055 and JP 61-020660 direct gas to the top of the nozzle. US 4778775 teaches injecting gas into the lower portion of a nozzle. These references do not attempt to shield the molten metal from gas.

Applicant respectfully requests substitution of the amended sheets for the corresponding sheets in the present application, and requests the written opinion be based on the amended claims.

Date: 3 Feb 2004

Vesuvius USA Corporation
27 Nobletown Road
Carnegie, PA 15106-1632
Tel: 412-276-1750 x252
Fax: 412-276-7252

Respectfully submitted,


James R. Williams
Reg. No. 43,268

1/2

BEST AVAILABLE COPY

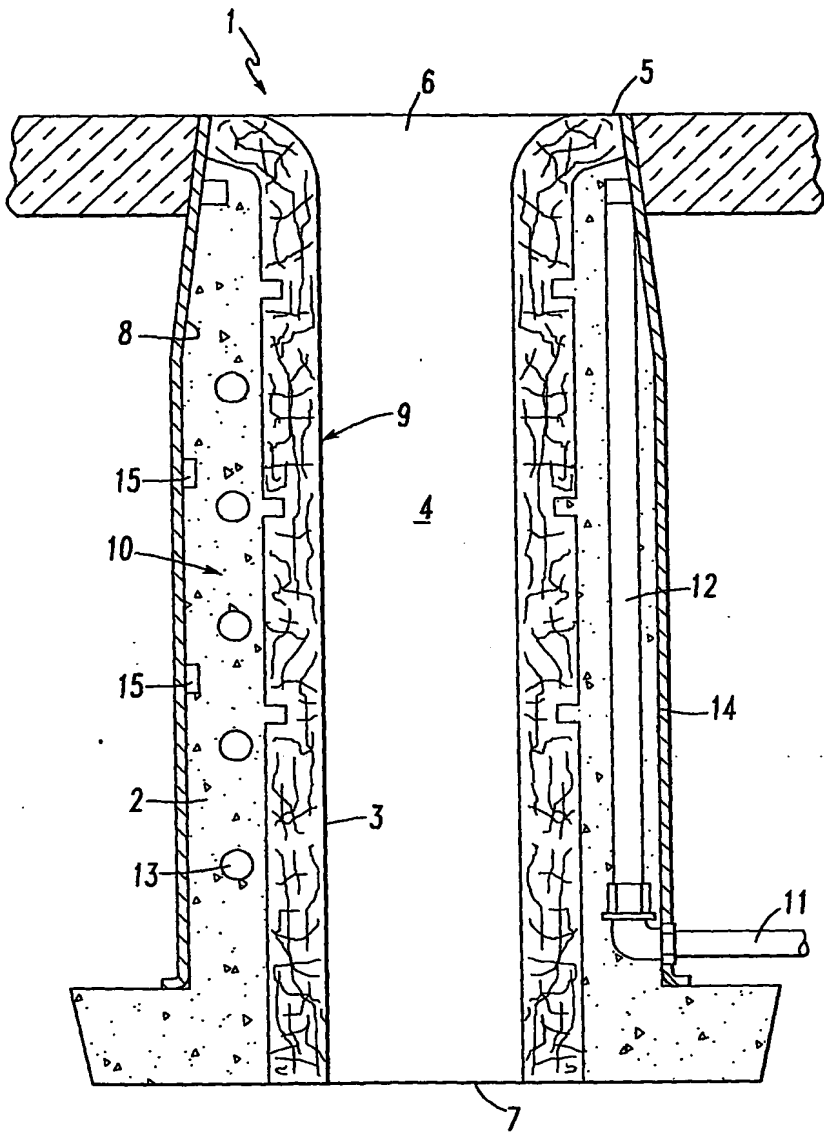


Figure 1

2/2

BEST AVAILABLE COPY

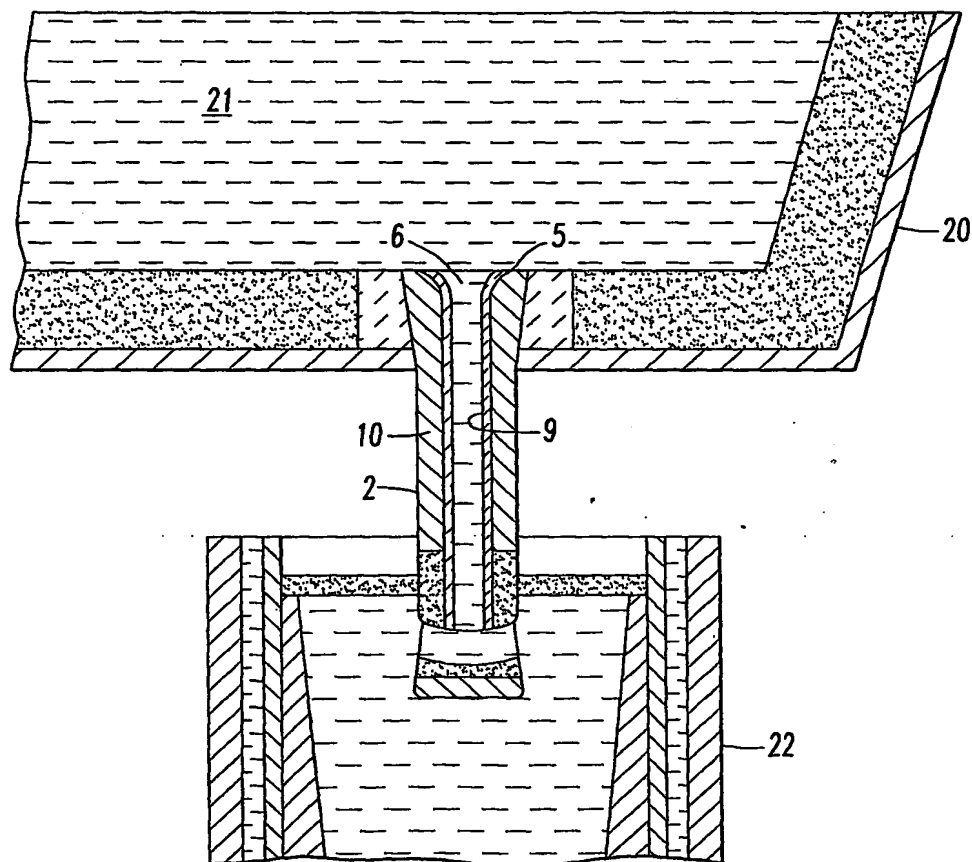


Figure 2

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/27209

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B22D41/54 B22D41/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B22D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 723 055 A (SIMOES JOSE ANTONIO FARIA ET AL) 3 March 1998 (1998-03-03) cited in the application column 3, line 38 -column 5, line 23; figures 1,2	1,2,4, 11-13
Y	----	7-9
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 171 (M-489), 17 June 1986 (1986-06-17) & JP 61 020660 A (TOSHIBA CERAMICS KK), 29 January 1986 (1986-01-29) abstract	1,11-13
Y	----	7-9
X	US 4 779 775 A (HIRAIWA YOSHITAKA ET AL) 25 October 1988 (1988-10-25) column 2, line 8 - line 56; figure 1 ----- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the International search

30 December 2003

Date of mailing of the International search report

14/01/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Maillliard, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27209

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 691 061 A (HANSE ERIC ET AL) 25 November 1997 (1997-11-25) claims 1-15; figures 2,3,5; example ----	7-9
A	WO 00 78484 A (NITZL GERALD ;CHADWICK ROBERT SCOTT (GB); FOSECO INTERNAT LTD (GB)) 28 December 2000 (2000-12-28) page 3, line 5 -page 5, line 22 page 10, line 6 - line 18; figure 1 ----	1-10
A	EP 0 399 407 A (VESUVIUS FRANCE SA) 28 November 1990 (1990-11-28) claims 1-10 -----	1-10

INTERNATIONAL SEARCH REPORT

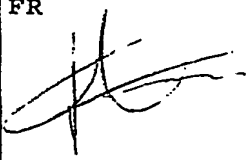
information on patent family members

International Application No.

PCT/US 03/27209

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5723055	A	03-03-1998	AT 199669 T	15-03-2001
			AU 709200 B2	26-08-1999
			AU 1114897 A	30-04-1997
			BR 9612628 A	16-07-2002
			CN 1203543 A ,B	30-12-1998
			CZ 9801071 A3	14-10-1998
			DE 69612110 D1	19-04-2001
			DE 69612110 T2	21-06-2001
			EP 0866739 A1	30-09-1998
			ES 2159366 T3	01-10-2001
			JP 11513617 T	24-11-1999
			PL 326167 A1	31-08-1998
			SK 46098 A3	11-01-1999
			TR 9800663 T2	21-07-1998
			WO 9713599 A1	17-04-1997
JP 61020660	A	29-01-1986	NONE	
US 4779775	A	25-10-1988	JP 7000227 B	11-01-1995
			JP 62050071 A	04-03-1987
			BE 905338 A1	16-12-1986
			BR 8603975 A	31-03-1987
			DE 3628066 A1	05-03-1987
			KR 9007115 B1	29-09-1990
			US 4867932 A	19-09-1989
US 5691061	A	25-11-1997	FR 2721241 A1	22-12-1995
			FR 2727340 A1	31-05-1996
			AT 169535 T	15-08-1998
			AU 697401 B2	08-10-1998
			AU 2795995 A	05-01-1996
			BR 9506265 A	12-08-1997
			CA 2169472 A1	21-12-1995
			CN 1129413 A ,B	21-08-1996
			CZ 9600428 A3	11-09-1996
			DE 69504027 D1	17-09-1998
			DE 69504027 T2	01-04-1999
			EP 0721388 A1	17-07-1996
			ES 2122636 T3	16-12-1998
			WO 9534395 A1	21-12-1995
			JP 9503445 T	08-04-1997
			RU 2146186 C1	10-03-2000
			CA 2206792 A1	06-06-1996
			CN 1167453 A ,B	10-12-1997
			WO 9616758 A1	06-06-1996
			JP 10510474 T	13-10-1998
WO 0078484	A	28-12-2000	AU 5542700 A	09-01-2001
			WO 0078484 A1	28-12-2000
EP 0399407	A	28-11-1990	FR 2647105 A1	23-11-1990
			EP 0399407 A1	28-11-1990
			JP 3005388 A	11-01-1991
			US 5094692 A	10-03-1992

VIII-4-1	<p>Declaration: Inventorship (only for the purposes of the designation of the United States of America)</p> <p>Declaration of Inventorship (Rules 4.17(iv) and 51bis.1(a)(iv)) for the purposes of the designation of the United States of America:</p>	<p>I hereby declare that I believe I am the original, first and sole (if only one inventor is listed below) or joint (if more than one inventor is listed below) inventor of the subject matter which is claimed and for which a patent is sought.</p> <p>This declaration is directed to the international application of which it forms a part (if filing declaration with application).</p> <p>I hereby declare that my residence, mailing address, and citizenship are as stated next to my name.</p> <p>I hereby state that I have reviewed and understand the contents of the above-identified international application, including the claims of said application. I have identified in the request of said application, in compliance with PCT Rule 4.10, any claim to foreign priority, and I have identified below, under the heading "Prior Applications," by application number, country or Member of the World Trade Organization, day, month and year of filing, any application for a patent or inventor's certificate filed in a country other than the United States of America, including any PCT international application designating at least one country other than the United States of America, having a filing date before that of the application on which foreign priority is claimed.</p>
VIII-4-1 -1	Prior applications:	60/407,815, US, 03 September 2002 (03.09.2002)

		<p>I hereby acknowledge the duty to disclose information that is known by me to be material to patentability as defined by 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the PCT international filing date of the continuation-in-part application.</p> <p>I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.</p>
VIII-4-1 -1-1 VIII-4-1 -1-2 VIII-4-1 -1-3 VIII-4-1 -1-4 VIII-4-1 -1-5 VIII-4-1 -1-6	Name: Residence: (city and either US State, if applicable, or country) Mailing address: Citizenship: Inventor's Signature: (if not contained in the request, or if declaration is corrected or added under Rule 26ter after the filing of the International application. The signature must be that of the inventor, not that of the agent) Date: (of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26ter after the filing of the International application)	RICHAUD, Johan Dundas, Canada 6 Waterwheel Crescent FR  August 26 th 2003